

4

**CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER**

DTIC FILE COPY

CRDEC-TR-88092

AD-A197 705

**REVIEW OF POLYMERIZATION AND PROPERTIES
OF AMINOALKYL ACRYLATES AND AMINOALKYL
METHACRYLATES**

by **Seok H. Hong, Ph.D.
Vincent M. McHugh**
RESEARCH DIRECTORATE

Sponsored by the U.S. Army Foreign Science and Technology Center,
Project 1Y665709 D650 (FSTC Project 40006).

July 1988

**DTIC
ELECTE**
S **D**
AUG 16 1988
E

**U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND**



Aberdeen Proving Ground, Maryland 21010-5423

This document has been approved
for public release and sale in
distribution is unlimited.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

Distribution Statement

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC-TR-88092			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION CRDEC		6b. OFFICE SYMBOL (if applicable) SMCCR-RSC-P		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION FSTC		8b. OFFICE SYMBOL (if applicable) AIFI-MB		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 220 Seventh St., NE Charlottesville, NC 22901-5396			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO. 1Y665709- D650	TASK NO. 4Q006
11. TITLE (Include Security Classification) Review of Polymerization and Properties of Aminoalkyl Acrylates and Aminoalkyl Methacrylates					
12. PERSONAL AUTHOR(S) Hong, Seok H., Ph.D., and McHugh, Vincent M.					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 85 Dec to 87 Dec		14. DATE OF REPORT (Year, Month, Day) 1988 July	
15. PAGE COUNT 23					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Aminoalkyl acrylate Alkyl acrylate Aminoalkyl methacrylate Polymerization Alkyl methacrylate (continued on reverse)		
FIELD	GROUP	SUB-GROUP			
07	03,04				
11	03,08,09				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The foreign literature of copolymers containing aminoalkyl acrylates and aminoalkyl methacrylates was reviewed with emphasis on ultrahigh molecular weight polymers. Additional emphasis was placed on polymerization methods and properties of the polymers. This literature review is limited to the time period 1970-1985.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL SANDPA J. JOHNSON			22b. TELEPHONE (Include Area Code) (301) 671-2914		22c. OFFICE SYMBOL SMCCR-SPS-T

UNCLASSIFIED

18. SUBJECT TERMS (continued)

Molecular weight
Polyelectrolyte complex
Configuration
Copolymer properties, *DEK*

PREFACE

The work described in this report was authorized under Project No. 1Y665709D650, CB Defense Data Collection and Systems Science. This work was started in December 1985 and completed in December 1987.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the Commander, U.S. Army Chemical Research, Development and Engineering Center (CRDEC), ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, Maryland 21010-5423. However, the Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for U.S. Government purposes.

This report has been approved for release to the public.

Acknowledgments

The authors thank Wendel J. Shuely and Brian S. Ince for their help in preparing this manuscript. We appreciate the assistance with computer-aided data and text processing provided by Stella C. Matthews. We also thank the staff of the Technical Library, CRDEC, for their assistance in obtaining the articles reviewed in this report.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



Blank

CONTENTS

	Page
1. INTRODUCTION	7
2. DISCUSSION	7
3. CONCLUSION	18
LITERATURE CITED	21

Blank

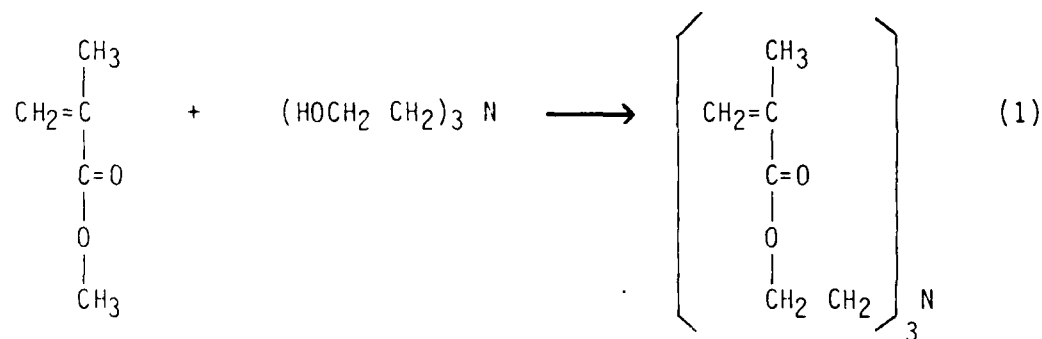
REVIEW OF POLYMERIZATION AND PROPERTIES OF AMINOALKYL ACRYLATES AND AMINOALKYL METHACRYLATES

1. INTRODUCTION

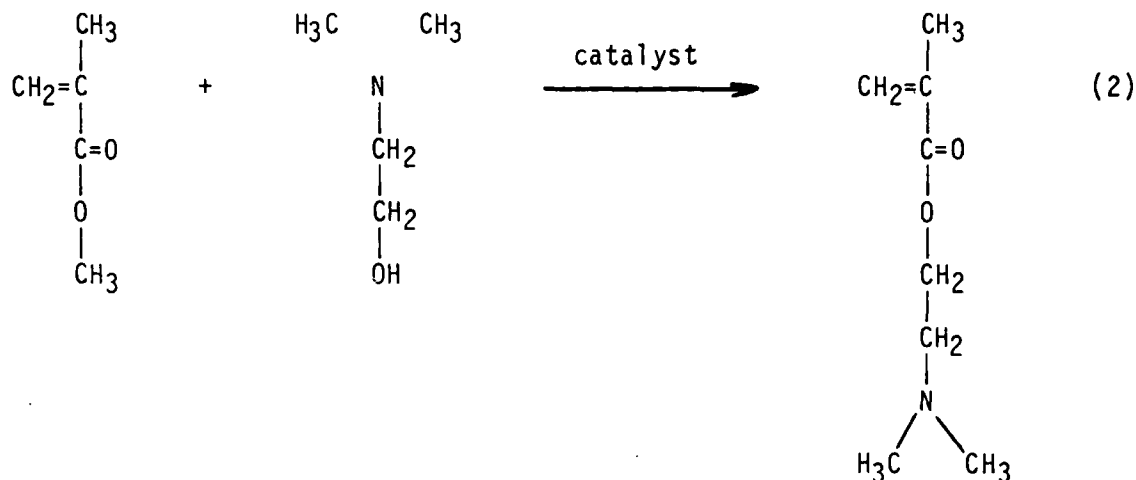
The purpose of this review is to identify commercially available alkyl methacrylate-co-alkylaminoalkyl methacrylate copolymers with an emphasis placed on ultrahigh molecular weight (MW) polymers of over 1 million daltons (i.e., megadalton polymers). The scope of this review might be limited to polymers produced by emulsion polymerization; however, many polymer properties are somewhat independent of MW or can be extrapolated from MW data, therefore, other polymerization methods are not excluded. The scope of this review is limited to foreign literature because polymerization and properties of domestic, commercially manufactured polymers were adequately reviewed by the authors.

2. DISCUSSION

A German patent was granted to Russian investigators Korshunov, Bodnaryuk, and Kut'in, in 1975.² The patent concerned the synthesis of methacrylate monomers containing an amino group through transesterification. These researchers used alkyl methacrylates, mainly methyl methacrylate (MMA), as precursors for the synthesis. For example, as shown in equation 1, MMA was reacted with triethanolamine in the presence of di- β -naphthol as a catalyst to yield tri(β -methacryloyl ethyl)amine. The number of hydroxyl groups in the amine could be varied to afford different degrees of substitution. For example, methyldi(β -methacryloyl ethyl)amine was obtained when methyldiethanolamine was used instead of triethanolamine.



A Japanese patent of 1984 described a similar method to prepare acrylic esters and methacrylic esters that contain an amino group by transesterification with aminoalcohols. This method used various catalysts.³ One of the examples given by the authors was the preparation of N,N-dimethylaminoethyl methacrylate (DMAEMA) from MMA and N,N-dimethylaminoethanol as shown in equation 2.



A study of bulk polymerization of N,N-dimethylaminoethyl acrylate (DMAEA) and DMAEMA was conducted in 1970 by Mal'tseva.⁴ DMAEA and DMAEMA were polymerized in the presence of 2,2'-azobisisobutyronitrile (AIBN) at 50, 60, 70, and 80 °C. In addition, the copolymerization of N,N-dialkylaminoethyl methacrylates with acrylonitrile (AN) was studied. The resulting nitrogen containing polymers were soluble in methanol and were precipitated in a 1:1 mixture of acetone and diethyl ether. The total activation energies for the ester monomers were calculated from a rate study. Infrared (IR) spectra were examined for the esters as well as for the resulting polymers.

In 1971, Kirillov and co-workers of the Union of Soviet Socialist Republics (USSR), reported a successful copolymerization of butyl methacrylate (BMA) with methacrylic acid (MAA) by an emulsion polymerization technique.⁵ The authors found that the viscosity of the copolymer solutions decreased when the initiator concentration or reaction temperature was increased. The BMA-co-MAA copolymer was linear and soluble in a mixture of 50% butyl acetate, 10% ethanol, 20% n-butanol, and 20% benzene. The viscosity, pH, specific viscosity versus rate of stirring, and moisture content of this copolymer were determined.

Solution polymerization of alkyl methacrylates and acrylic anhydrides using anionic initiators was reported in 1972.⁶ A German patent by Lewis and Haggard of Rohm and Haas Company documented the synthesis of homo- and co-polymers of alkyl methacrylate with MW ranges of 500-100,000. These polymers were soluble in organic solvents. The researchers characterized these polymers using thermal gravimetric analysis, IR, gel permeation chromatography (GPC), and carboxylic acid titration.

Yeliseyeva of Russia reported the emulsion polymerization of various alkylacrylates.⁷ The author prepared stable lattices by copolymerization of alkylacrylates and an ionizable monomer soluble in water without any emulsifier. Examples of the ionizable monomers used are MAA or the salt of DMAEMA. Persulphate was used as an initiator. A dilatometric study of the kinetics of copolymerization of BMA with DMAEMA at monomer feed ratios of 85:15 and 70:30 showed that the rate of the process changed as copolymerization proceeded; at the first stage, the rate was considerably lower than at the next stage. This was explained by the author as follows: water soluble

DMAEMA is polymerized in the first stage; thus, copolymers arising in this first stage of copolymerization are enriched with DMAEMA. This means that copolymerization begins in an aqueous solution in spite of the very low water solubility of BMA. The kinetic rate increase observed as conversion increased during polymerization (without an emulsifier) is explained by the transition of the process from an aqueous solution into polymer-monomer particles.

In a 1974 article of a Russian journal, Ryabov and co-workers reported the synthesis of poly(BMA) and copolymers of butyl acrylate (BA) and MMA.⁸ These polymers, obtained using solution polymerization techniques, were linear and soluble in toluene. The Newtonian viscosity of the films versus applied stress and temperature were measured.

In 1974, Gerber and his co-workers reported copolymerization of BMA with aminoalkyl methacrylates (AmAMA) including DMAEMA.^{9,10} Polymerization of BMA and copolymerization of BMA with AmAMA were carried out by solution polymerization in toluene with AIBN as the initiator. Petroleum ether was the non-solvent for these polymers, and these polymers were purified by reprecipitation in a toluene and petroleum ether mixture. A typical copolymer had an MW of 0.2 megadalton, and the aminoester units (~3%) were distributed uniformly throughout the polymer chains. Films of these polymers were applied to steel, and their corrosion protection properties were characterized by a capacitance-ohmic method in a humidity chamber. The copolymers containing aliphatic amino groups showed better protective properties than either the homopolymer of BMA or copolymers containing aromatic or heterocyclic amino groups.

In 1975, Japanese researchers Matsumoto, Oshibo, and Onoe published an article concerning the effect of poly(DMAEMA) on decomposition of potassium persulphate.¹¹ The poly(DMAEMA) and poly(acrylamide-co-DMAEMA) were prepared by solution polymerization at 70 °C for 48 hr using AIBN as the initiator and benzene and dioxane as the respective solvents. The limiting viscosity numbers (LVN) of the polymers were determined using a Cannon-Ubbelohde viscometer. The composition of the poly (acrylamide-co-DMAEMA) was determined from the DMAEMA content of the polymer by titration with hydrochloric acid.

A study of block copolymerization of DMAEMA with several vinyl monomers was conducted by Gerdvilyte and his co-workers.¹² The vinyl monomers that were investigated included vinyl acetate (VA), MMA, and BMA. Copolymerization was conducted with the initiator AIBN. The resulting copolymers, poly(MMA-co-DMAEMA) and poly(DMAEMA-co-VA), were soluble in benzene and toluene, respectively, and insoluble in heptane. Copolymerization was examined as a function of such reaction conditions as the amount of initiator, reaction temperature and duration, and molar composition of the initial monomer mixture. As a result, it was shown that during copolymerization of DMAEMA and VA, the latter comonomer was less reactive, whereas MMA, BMA, and DMAEMA reactivity levels were virtually the same.

In 1976, Golenger and co-workers published their results on the study of parameters of thermodynamic interaction between cellulose diacetate (CD) and several polymers including poly(VA), poly(diethylaminoethyl methacrylate), (DEAEMA), and poly(vinyl pyrrolidone), (VP).¹³ Several characteristics of the polymers investigated are presented in Table 1.

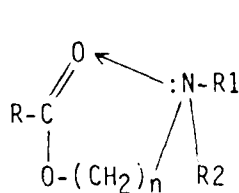
Table 1. Physical and Solvent Properties of Several Polymers at 25 °C

Polymer	Solvent	LVN* (dl/g)	Density (g/cm ³)	Hildebrand Solubility Parameter (cal/cm ³) ^{0.5}
CD	Acetone	1.5	1.33	12.1
poly(VA)	Acetone	1.1	1.2	9.1
Poly(DEAEMA)	Acetone	0.32	1.11	9.4
poly(VP)	Acetic acid	0.9	1.27	12.6

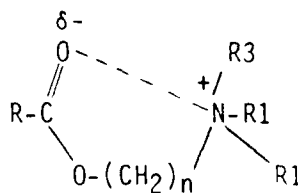
*limiting viscosity number.

Using Flory-Huggins parameters and Scott's theory, the authors proved that the nature of the solvent has a very significant influence on the thermodynamic stability of multicomponent polymer systems.

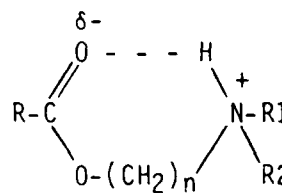
Two Russian researchers, Bogatkov and Cherkasova, investigated the effect of the structure of amino esters on the rate of their alkaline hydrolysis.¹⁴ The researchers knew that amino esters in base form (unprotonated) are hydrolyzed faster than their analogues without amino groups, and the rate of alkaline hydrolysis is increased by quaternization of amino groups. Furthermore, the hydrolysis rate for the protonated amino esters was greater than that of quaternized forms. The authors explained that these occurred as a result of inductive, steric, and electrostatic effects; that is, "the influence of the neutral amino group (unprotonated) is a sum of inductive and steric effects, and that of quaternary ammonium salts is a sum of inductive, steric, and electrostatic effects." The contributions of inductive effect for the base forms of amino esters were rather small and increased with quaternization. The inductive effect, however, was dependent on the distance between carbonyl group and amino groups. Therefore, the electrostatic effect became more important when this distance increased. The schematic representations of these interactions are shown below.



I



II



III

The inductive effect of amino groups in the base form is represented by (I); (II) represents the dipole-dipole type electrostatic interaction in the quaternized form, and (III) represents intramolecular hydrogen bonding in the protonated form of amino esters. The authors postulated that the hydrogen bond type of interaction in the protonated amino esters is stronger than the dipole-dipole type of interaction in the quaternized amino esters. This result explains the greater hydrolysis rate in the protonated forms. The amino esters used in this investigation were limited to monomeric esters.

A U.S. patent was granted to Hrabak, Bezdek, Hynkova, and Bouchal of Czechoslovakia in 1978.¹⁵ This patent claims that polymers or copolymers that contain covalently bound tertiary amino groups that are soluble or meltable can be converted into insoluble, cross-linked polymers by ultraviolet (UV) or visible light in the presence of a halogen compound. The polymers containing tertiary amino groups included DMAEMA, DEAEMA, and copolymers of these with styrene. The authors reported that the density of the cross links formed between polymeric chains could be controlled by the number of tertiary amino groups built into the chain as well as the amount of the halogen compound employed. Consequently, as the number of the tertiary amino groups in a polymeric molecule was increased, the density of the cross links increased; and insoluble connected macromolecules were obtained. However, neither the structure of the cross-linked polymers nor the mechanism of the cross-linking was mentioned.

In a 1978 Japanese patent, Moriga described a method for stabilization of poly(amino acrylate) solutions.¹⁶ The method of polymerization was solution polymerization. Solvents used were N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP), dioxane, acetone, and lower MW alcohols. In this invention, amino acrylate compounds included dialkylaminoethyl acrylates such as DMAEA and diethylaminoethyl acrylate (DEAEA), and dialkylaminoethyl methacrylates such as DMAEMA and DEAEMA.

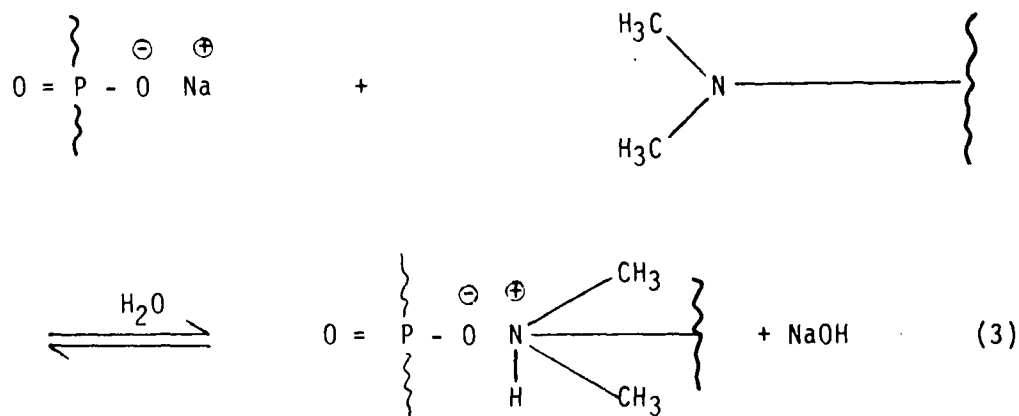
A synthesis and study of aminoalkyl acrylate polymers and copolymers were conducted by Gerdvilyte in 1979.¹⁷ The kinetics of polymerization of DMAEMA and 1,3-bis(dimethylamino)isopropyl methacrylate (BDIMA) and copolymerization of the above with acrylate comonomers such as MMA, BMA, and VA were studied dilatometrically or by the ampoule method using AIBN as the initiator. The resulting homo- and copolymers had MWs of 400-8,000 daltons. From the kinetic data, the activation energies were calculated to be 19.2 and 20.63 Kcal/mole for DMAEMA and BDIMA, respectively. Also reported were the reactivity ratios of the aminoalkyl methacrylates with MMA, BMA, VA, and styrene. The osmometric and viscometric studies of the polymer solutions were conducted as well. As a result, Mark-Houwink coefficients were calculated as well as reactivity ratios of these monomers, which are given in Table 2.

Table 2. Reactivity Ratios (r_1 , r_2) of Aminoalkyl Methacrylates and Other Vinyl Monomers

Monomer1	Monomer2	r_1	r_2
DMAEMA	MMA	0.717	0.676
DMAEMA	BMA	0.705	0.66
BDIMA	MMA	0.612	0.502
BDIMA	BMA	1.233	0.645
BDIMA	styrene	0.33	1.017
BDIMA	VA	1.519	0.267

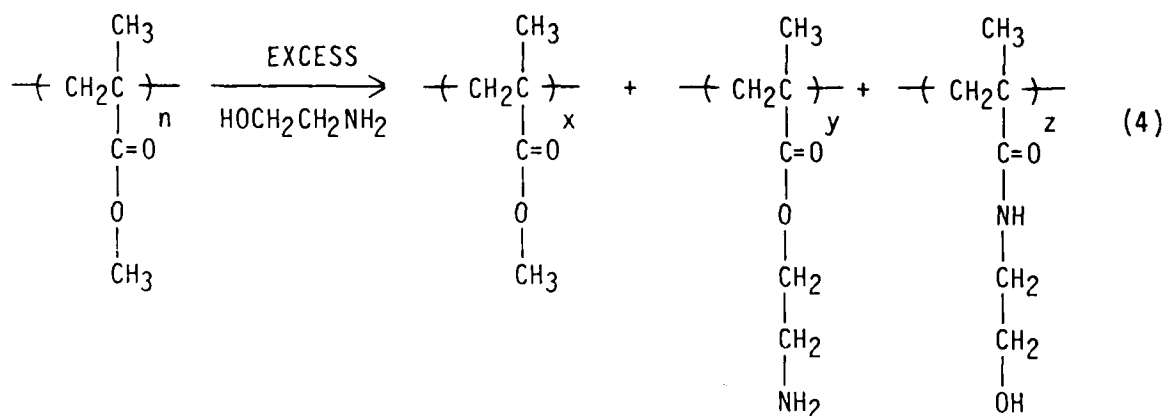
Izumrudov and colleagues at M.V. Lomonosov State University of USSR studied the behavior of non-stoichiometric polyelectrolyte complexes in aqueous salt solutions.¹⁸ The polyelectrolytes studied were poly(MAA), poly(4-vinyl-N-ethylpyridinium bromide), poly(DMAEMA), poly(AA), and sodium polyphosphate. Preparatory ultracentrifugation and sedimentation studies were done to determine the composition of insoluble polyelectrolyte complexes. The content of polycomplex components in the supernatant liquid was determined by various methods appropriate for the particular polymer. For example, potentiometric titration was employed for poly(DMAEMA). Researchers showed that with an increase in the ionic strength of the solution, the dimensions of polycomplex particles and second virial coefficients of their solutions decreased. On reaching a given salt concentration in the solution of nonstoichiometric polycomplex, phase separation took place with a stoichiometric complex in the concentrated phase.

Researchers of M.V. Lomonosov University of USSR studied water-soluble polyelectrolyte complexes formed by the interaction between high MW poly(DMAEMA) and polyphosphates or polyacrylates in 1981.¹⁹ In this study, researchers showed that the degree of transformation in the reaction between polyelectrolytes is the most important parameter determining solubility, composition, structure, and properties of polyelectrolyte complexes. An example of the salt formed as a result of the reaction between poly(DMAEMA) and polyphosphate is shown in equation 3.



The equilibrium of the reaction may be displaced to the right by neutralizing the alkaline sodium hydroxide produced as a result of this reaction. Results of another study on this subject were published in 1981.²⁰ The authors studied the equilibria in the reactions between high MW poly(DMAEMA) and oligo- and polyphosphates. These equilibria described the reversible association of the chemically complementary macromolecules (equilibrium I) and the reversible chemical reaction between links of oppositely charged polyelectrolytes (equilibrium II). Researchers showed that the oligo- and polyphosphates are uniformly distributed between the polycationic macromolecules. Researchers also found that the reaction between the two high MW polymers can be satisfactorily described in terms of equilibrium II alone, whereas the interactions between oligomeric molecules and high MW polymer chains can be described in terms of equilibrium I; that is, the latter interactions occur by the successive addition of individual oligomeric molecules to the high MW poly(DMAEMA) chains.

In 1981, Zil'berman and co-workers of USSR studied the modification of poly(MMA).²¹ They produced water-soluble copolymers by the interaction of poly(MMA) and ethanolamine. When poly(MMA) and ethanolamine, in a molar ratio of 1:1, were used, the resulting polymer did not dissolve in water but swelled in it. The authors reasoned that this occurred as a result of the reaction of ethanolamine molecules with poly(MMA) through their amino group and their hydroxyl group and led to cross-linking of the polymer. When the researchers used an excess of ethanolamine (1:5 molar ratio), they produced water-soluble copolymers that consisted of three types of repeating units, as shown in equation 4. The resulting ratio of the three repeating units in the copolymer was dependent on reaction time.



Shul'ga and co-workers of USSR investigated cooperative inter-macromolecular reactions in 1982.^{22,23} They used lignosulphonates, a water-soluble derivative of a natural polymer lignin, and high MW polybase, poly(DMAEMA). The researchers showed that the reactions took place by electrostatic interaction between sulpho groups of lignosulphonates and amino groups of poly(DMAEMA). The authors concluded that, similar to reactions between synthetic linear polyelectrolytes of opposite charge, these were cooperative reactions and were dependent, to a large extent, on the MW of lignosulphonates.

A European patent was granted to Lorenz, Murphy, and Rutherford of GAF Corporation in 1983.²⁴ This patent concerns the preparation of ter-polymers containing vinyl caprolactam (VCL), vinyl pyrrolidone (VP), and aminoalkyl acrylates including DMAEMA and DEAEMA.

Russian investigators²⁵ studied the polymerization of quaternary salts of DMAEMA. Monomeric quaternary salts were prepared by using DMAEMA with propyl iodide (PI) or allyl iodide (AI). Polymerization of the resulting quaternary salt of DMAEMA was conducted at different temperatures in the presence of AIBN. The reaction was conducted in sealed ampoules with DMF, 95% ethanol, or DMSO as the solvent. Researchers learned that the low temperature polymerization of the quaternary salts of DMAEMA with PI in the presence of AIBN had the appearance of a redox initiation, and the monomeric salt served as the reducing agent. The viscosity of the resulting polymers were measured.

The graft polymerization of DMAEMA to polycaproamide (PCA), which took place at elevated temperatures ($>70^{\circ}\text{C}$), was investigated by Khardin and co-workers.²⁶ The initiating system of $\text{Cu}^{2+}-\text{H}_2\text{O}_2$ formed a radical on the PCA chain, and the radical initiated the graft polymerization of DMAEMA. This method of producing graft PCA copolymers was recommended by the authors because of the high grafting efficiency.

Topchiyev, Ruzinyev, and Dzhililov of USSR studied the polymerization of aminoalkyl methacrylates, including DMAEMA and DEAEMA.²⁷ A spontaneous polymerization reaction was observed in solutions of aminoalkyl methacrylate in various organic solvents such as ethanol, DMF, and DMSO in the presence of various alkyl halides (ethyl bromide, propyl bromide, isopropyl chloride, etc.). The resulting polymer was isolated by precipitation from diethyl ether and various physical and chemical properties were studied. Some of the findings were as follows:

- The MW of the polymer did not change in the course of polymerization; that is, MW was not dependent on the degree of conversion.
- The MW of the resulting polymer increased with greater initial concentration of monomeric quaternary salt in the reaction system, with other conditions being equal.
- The presence of a very small quantity of acetic acid resulted in a sharp decrease in the MW of the resulting polymers. This reaction indicated that the nature of the polymerization was nonradical and may have been anionic.

Poly(DMAEMA) and other polyelectrolytes were investigated by Asanov, Il'yasov, Akhmedov, and Saidov of USSR in 1984 to produce stable aqueous sulfur suspensions.²⁸ The most stable sulfur suspension, with the addition of poly(DMAEMA), occurred with a mixing time of 15-60 min. The stabilizing effect of polyelectrolyte additions was reported to be related to the fact that their molecules, forming an adsorption layer, increased the bonding between the solid body particles and the surrounding liquid. In addition, the reduced stability of the sulfur suspension with prolonged mixing appeared to be caused by the disintegration of the adsorption layer.

Pradny, Sevcik, and Vlcek of Czechoslovakia studied the solution polymerization of DMAEMA in 1984.²⁹ The authors employed anionic polymerization techniques to produce a linear, stereoregular (syndiotactic) polymer, which was soluble in an ethanol-water mixture and which had an MW of 0.03 megadalton. This paper described the kinetics of quaternization of poly(DMAEMA), with various tacticity, by methyl iodide. Also, the reactivity of this polymer was compared with the reactivity of the lower MW model compound, 2-(N,N-dimethylamino)ethyl pivalate. In 1985, Pradny and Sevcik extended this research.³⁰ These authors determined the dissociation constants of partially ionized isotactic and atactic poly(DMAEMA) in water-ethanol solutions.

In 1985, Kolokol'kina and co-workers of USSR conducted an investigation of synthetic methods for graft copolymers of cellulose containing quaternary ammonium groups and their antimicrobial properties.³¹ These graft copolymers of cellulose were prepared by using cotton fabric and quaternary ammonium salt forms of DMAEMA and DEAEMA.

A summary of these papers is presented in Table 3.

Table 3. Polymerization and Properties of Copolymers Containing Aminoalkyl Acrylates and Aminoalkyl Methacrylates

Monomers	Method of Polymerization	Copolymer Properties				Literature cited
		MW (daltons)	Solvents	Config	Other	
DMAEMA, ^a DMAEA, ^b AN ^c	bulk (radical)	--	methanol	linear	IR	4
BMA ^d MAA ^f	emulsion	--	solvent 'A' ^e	linear	viscosity, pH	5
AlkMA, ^g acrylic anhydrides	solution (anionic)	500 to 100,000	organic solvents	linear	TGA, IR, GPC, titration	6
DMAEMA, BMA	emulsion	--	benzene	--	dilatometry, kinetic data	7
BMA, BA, ^h MAA	solution	--	toluene	linear	viscosity	8
BMA, AmAMA ⁱ	solution (radical)	200,000	toluene, methanol	linear	coating properties	9, 10
DMAEMA, acrylamide	solution	--	benzene, dioxane	linear	viscosity, titration	11
DMAEMA, BMA, VA, ^j MMA ^k	solution (radical)	--	benzene, toluene	--	kinetic data	12
DEAEMA, VA, VP ^l	--	--	acetone	graft (on CD ^m)	viscosity	13
DEAEMA, DMAEMA, AlkMA, styrene	--	300,000	benzene, chloroform	linear to cross-link	--	15
AmAMA, AmAA, ^o AlkA, ^p AlkMA	solution (radical)	--	DMF, NMP, ⁿ DMSO, acetone, dioxane	linear	viscosity, stability	16
DMAEMA, VA, BDIMA, ^q MMA, BMA	solution (radical)	400 to 8,000	--	--	--	17

Table 3. Polymerization and Properties of Copolymers Containing Aminoalkyl Acrylates and Aminoalkyl Methacrylates (continued)

Monomers	Method of Polymerization	Copolymer Properties				Literature cited
		MW (daltons)	Solvents	Config	Other	
MMA, AA, ^r DMAEMA, vinyl pyridine, polyphosphates	--	--	water	linear	ultra-centrifuge, sedimentation	18
DMAEMA	solution (radical)	500,000	benzene	linear	polyelectrolyte complexes	19
DMAEMA	bulk (photo-chemical)	1,000,000	--	linear	titration, sedimentation	20
DMAEMA	radical	500,000	--	linear	titration	21
VP, VCL, ^s DMAEMA, DEAEMA	--	--	water, ethanol	linear	--	24
DMAEMA salts	solution (radical)	--	DMF, DMSO, water, ethanol	linear	intrinsic viscosity	25
DMAEMA	solution (redox: Cu ²⁺ -H ₂ O ₂)	--	--	graft	--	26
DMAEMA, DEAEMA	thermal-spontaneous	--	ethanol, DMSO, DMF	--	kinetic study by NMR	27
DMAEMA	--	--	water	linear	--	28
DMAEMA	solution	30,000	THF, ethanol/ water	linear: stereoregular (isotactic, syndiotactic, and atactic)	--	29

Table 3. Polymerization and Properties of Copolymers Containing Aminoalkyl Acrylates and Aminoalkyl Methacrylates (continued)

Monomers	Method of Polymerization	Copolymer Properties				Literature cited
		MW (daltons)	Solvents	Config	Other	
DMAEMA, DMABMA ^a	--	--	ethanol/water	--	viscosity, titration	29
DMAEMA, DEAEMA (salt form)	--	--	--	graft	--	30

^aN,N-dimethylaminoethyl methacrylate.

^bN,N-dimethylaminoethyl acrylate.

^cacrylonitrile.

^dbutyl methacrylate.

^ea mixture of 50% butyl acetate, 10% ethanol, 20% n-butanol, and 20% benzene.

^fmethacrylic acid.

^gvarious alkyl methacrylates.

^hbutyl acrylate.

ⁱvarious aminoalkyl methacrylates.

^jvinyl acetate.

^kmethyl methacrylate.

^lvinylpyrrolidone.

^mcellulose diacetate.

ⁿN-methylpyrrolidone.

^ovarious aminoalkyl acrylates.

^pvarious alkyl acrylates.

^q1,3-bis(dimethylamino)isopropyl methacrylate.

^racrylic acid.

^svinyl caprolactam.

^t4-(N,N-dimethylamino)butyl methacrylate.

3. CONCLUSION

Aminoalkyl methacrylates and acrylates are readily polymerizable monomers that render a way of incorporating pendant amino groups into polymeric systems. The resulting polymers possess cationic properties, especially when the tertiary amine is quaternized. The presence of pendant amino groups can improve the properties of the resulting copolymers, such as improving the binding of polymers to a variety of materials, increasing compatibility with other polymer systems, and increasing thermal stability or dyeability.

The aminoalkyl methacrylates and acrylates, due to their availability and their polymerizability, were investigated by various researchers in a wide range of foreign countries. The solubility of these polymers in water and various organic solvents added to their importance. The resulting polyelectrolytes have a wide range of practical as well as theoretical applications.

Blank

LITERATURE CITED

1. Hong, S.H., and McHugh, V.M., Review of Preparation and Properties of Polymers from Copolymerization of Aprotic Acrylic Monomers with Protic Acrylic Monomers, CRDEC-TR-88093, U.S. Army Chemical Research, Development and Engineering Center, July 1988, UNCLASSIFIED Report.
2. Korshunov, M.A., Bodnaryuk, F.N., and Kut'in A.M., German Patent DE 1543279, 1975.
3. Shibatage, K., Japanese Patent 57-206639, 1982.
4. Mal'tseva, L.V., "Bulk Polymerization of Beta-(diethylamino) ethyl Acrylates," Uzb. Khim. Zhurn. Vol. 13 (2), p 56 (1969).
5. Kirillov, A.I., Krymova, A.I., Matina, T.A., and Deryabina, R.A., "Emulsion Copolymerization of Butyl Methacrylate with Methacrylic Acid," Plast. Massy. Vol. 10, p 5 (1971).
6. Lewis, S.N., and Haggard, R.A., German Patent 2218836, 1972.
7. Eliseeva, V.I., "Possible Mechanism of Particle Formation in Emulsion Polymerization Without an Emulsifier," Chem., Phys. Chem. Anwendungstech. Grenzflaechenaktiven Stoffe, Ber. Int. Kongr., 6th, Vol. 1, p 361 (1973).
8. Ryabov, A.V., Malysheva, T.S., Smirnova, L.A., Zamotova, A.V., and Shevchuk, L.M., "Viscosity and Strength Properties of Polyacrylate Films Formed on a Water Surface," Zhurnal Prikladnoi Khimii. Vol. 47 (8), p 1842 (1974).
9. Gerber, V.D., and Eliseeva, V.I., "The Effects of Functional Groups of Various Chemical Nature on the Film-Forming Properties of Acryl Polymers," Lakokrasoch. Mater. Ikh. Primen. Vol. 4 (1970).
10. Gerber, V.D., Eliseeva, V.I., Zhigalova, K.A., and Rozenfel'd, I.L., "Protective Properties of Acrylic Copolymer-Containing Coatings Containing Inhibiting Groups," Zashch. Metal. Vol. 10 (1), p 71 (1974).
11. Matsumoto, T., Okubo, M., and Onoe, S., "Suspensions and Emulsions, XXIII. Polymer Effect of Poly(dimethylaminoethyl methacrylate) on the Decomposition of Potassium Persulfate," Kobunshi Ronbunshu Vol. 32(6), p 333 (1975).
12. Gerdvilyte, B., Vaitkevicius, D., Katkus, A., and Macionis, Z., "The Study of Block Copolymerization of Dimethylaminoethyl Methacrylate with Several Vinyl Monomers," Vilinyus State University, VINITI Vol. 1, pp 3667-75 (1975).
13. Golender, B.A., Sagdiyeva, Z.G., Fuzailov, S.H., and Tashmukhamedov, S.A., "Parameters of Cellulose Diacetate Thermodynamic Interactivity with Certain Polymers," Vysokomol. Soyed., Ser. B., Kratkiye Soobshcheniya Vol. 9, p 688 (1976).

14. Bogatkov, S., and Cherkasova, E., "Quantitative Estimation of the Contribution of Individual Structural Effects in the Alkaline Hydrolysis Rate of Amino Alcohol Esters," Org. React. (Tartu) Vol. 14, p 165 (1977).
15. Hrabak, F., Bezdek, M., Hynkova, V., and Bouchal, K., U.S. Patent 4072805, 1978.
16. Moriga, H., Japanese Patent 78144949, 1978.
17. Gerdvilite, B., Deposited Document, "Synthesis and Study of Aminoalkyl Acrylate Polymers and Copolymers," VINITI Vol. 417, p 3784 (1979).
18. Izumrudov, V.A., Kharenko, O.A., Kharenko, A.V., Gulyaeva, Zh.G., Kasaikin, V.A., Zezin, A.B., and Kabanov, V.A., "Behavior of Nonstoichiometric Polyelectrolyte Complexes in Aqueous Salt Solutions," Vysokomol. Soedin., Ser. A. Vol. 22(3), p 692 (1980).
19. Kharenko, A.V., Neverova, E.A., Kalyuzhnaya, R.I., Zezin, A.B., and Kabanov, V.A., "Structure and Properties of Polyelectrolyte Complexes which are Products of Uncompleted Reactions Between Poly(N,N-dimethylaminoethyl methacrylate) and Salts of Polyphosphoric Acid and Poly(acrylic acid)," Vysokomol. Soedin., Ser. A. Vol. 23 (9), p 2083 (1981).
20. Kharenko, A.V., Kalyuzhnaya, R.I., Zezin, A.B., and Kabanov, V.A., "Two Types of Chemical Equilibriums in Reactions Between Polyelectrolytes," Vysokomol. Soedin., Ser. A. Vol. 23 (12), p 2657 (1981).
21. Zil'berman, E.N., Khitrin, S.V., Spasskaya, R.I., and Kuchina, T.P., "Production of Water-Soluble Polymers by Modification of PMMA with Amino-Alcohols," Vysokomol. Soedin. Kratkie Soobshcheniya, B. Vol. 23 (12), p 889 (1981).
22. Shul'ga, G.M., Kalyuzhnaya, R.I., Mozheiko, L.N., Rekner, F.V., Zezin, A.B., and Kabanov, V.A., "Cooperative Intermacromolecular Reactions with the Participation of Lignosulfonates," Vysokomol. Soedin., Ser. A. Vol. 24 (7), p 1516 (1982).
23. Sulga, G., Mozheiko, L.N., Rekners, F., Kalyuzhnaya, R.I., Zezin, A.B., and Kabanov, V.A., "Chemical Conversions in Lignosulfonate-Based Polyelectrolyte Complexes," Khim. Drev. Vol. 1, p 87 (1982).
24. Lorenz, D.H., Murphy, E.J., and Rutherford, J.M., European Patent 0074191A2, 1983.
25. Maksumov, A.S., Umarova, I.K., Dzhaliilov, A.T., and Kapriyelova, G.V., "Synthesis and Polymerization of Monomeric Quaternary Salt N,N-dimethylaminoethyl Methacrylate with Haloalkyls," Izvestiya Vysshikh Uchebnykh Zavedeniy: Khimiya i Khimicheskaya Tekhnologiya Vol. 8, p 981 (1983).
26. Khardin, A.P., Zheltobryukhov, V.F., and Tatarnikov, M.K., "Low-Temperature Synthesis of Graft Copolymers of Polycaproamide with Poly(dimethylaminoethyl methacrylate)," Khimicheskie Volokna Vol. 3, p 33 (1984).

27. Topchiyev, D.A., Ruziyev, R., and Dzhaliylov, A.T., "Some Characteristics of Polymerization of Aminoalkylmethacrylates," Uzbekskiy Khimicheskiy Zhurnal Vol. 4, p 37 (1984).

28. Asanov, A., Il'yasov, A., Akhmedov, K.S., and Saidov, P., "Effect of Certain Factors on the Stabilization of a Sulfur Suspension in the Presence of the Polyelectrolyte Poly(dimethylaminoethyl Methacrylate)," Dokl. Akad. Nauk. UZSSR Vol. 2, p 41 (1984).

29. Pradny, M., Sevcik, S., and Vlcek, P., "Precursors of Hydrophilic Polymers. 4. The Kinetics of Quaternization of Poly(2-dimethylaminoethylmethacrylate) with Methyl Iodide," Polym. Bull. (Berlin) Vol. 12(4), p 337 (1984).

30. Pradny, M., and Sevcik, S., "Precursors of Hydrophilic Polymers. 3. The Potentiometric Behavior of Isotactic and Atactic Poly(2-dimethylaminoethyl methacrylate) in Water/Ethanol Solutions," Makromol. Chem. Vol. 186, p 111 (1985).

31. Kolokol'kina, N.V., Penenzhik, M.A., Solovskii, M.V., Plotkina, N.S., Panarin, E.F., and Virnik, A.D., "Synthesis of Cellulose Graft Copolymers Containing Quaternary Ammonium Groups, and Study of Their Antimicrobial Properties," Zhurnal Prikladnoi Khimii Vol. 58(7), p 1603 (1985).